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Provenance analysis of porphyritic volcanic materials in San Diego using portable X-ray Fluorescence

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ABSTRACT

Geochemical research using aphanitic volcanic rocks such as basalt and obsidian has long contributed to archeological understanding. Porphyritic materials have proven less amenable to methods of compositional analysis largely due to their complex structure. Under some circumstances, similarities in structure can mask geochemical signatures indicative of localized formations. Fine-grained volcanic materials comprise the majority of lithic assemblages in San Diego County, California, yet include a wide variety of geologic formations that each contains rocks with similar structural features and quality for producing lithic tools. This combination of diversity and overlapping structure have led to a dominant assumption that materials were either locally procured from the nearest available source of tool stone, or attributed to the Santiago Peak Volcanic formation as a known source of high-quality fine-grained volcanic materials. This study investigates the potential for using pXRF for provenance research on fine-grained volcanic materials in southern California. Results indicate that volcanic materials can be suitably discriminated using pXRF that sourcing porphyritic volcanic materials is possible and can be applied to archeological assemblages.

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1. Introduction

Research into the utilization, transport, and trade of lithic artifacts has traditionally focused on exotic items, such as obsidian and cryptocrystalline silicates, which are not available within geological formations in proximity to a given archeological site. An approach focusing on exotic materials often includes an informal assumption, such that any materials similar to local geological formations must have their origins within those formations. Without verification, assumptions may serve to obscure more localized movements of peoples and lithic materials, and unintentionally bias research towards inferences of limited or localized patterns of land use in prehistory.

Analysis of obsidian and homogenous fine-grained volcanic (FGV) lithic materials using X-ray Fluorescence (XRF) has been repeatedly demonstrated as being useful for provenance research, while efforts using complex banded or porphyritic volcanic materials have been limited (Grave et al., 2012; Pollard et al., 2007; Potts and West, 2008; Shackley, 2011). San Diego presents a difficult challenge in respect to determining both material types and origins (Dietler, 2004). In San Diego County three major sources exist for locally derived volcanics with Santiago Peak Volcanics/Metavolcanics, Jacumba/Table Mountain Volcanics and the Lusardi Formation. Porphyritic materials from these formations generally have a fine-grained groundmass suitable for flaking, but vary in grain size, consistency, and phenocrysts of variable size and spacing within the matrix. The spacing of non-conformities and phenocrysts is frequently larger than the analytical volume (surface area and penetration depth) for XRF. While not the preferred homogeneous matrix, there appears to be suitable groundmass accessible for geochemical analysis.

The presence of multiple related volcanic formations of varying consistency and quality for producing functional lithic tools makes identifying patterns of lithic procurement and possible movements difficult. Generic categories of "volcanic" or made attempts at attributing sources, such as Santiago Peak, based solely on visual cues are pervasive in the San Diego region (Dietler, 2004). This may well be effective, but concerted efforts at demonstrating the effectiveness of these visual classifications have been lacking. There is also the problem of variation in the colors and characteristic grain structure within known geological formations in the region. Depending on the individuals' familiarity with San Diego area geology, the effective classification of materials will be limited. The basic question is whether or not another means of differentiating between different lithic material sources with similar visual and physical properties?

In the current study the overall goal was to examine the geochemical relationships and affinities between some of the more commonly occurring types of volcanic materials and to test the potential relationships between a lithic material typology based upon visual attributes as well as chemical affinities. Portable XRF (pXRF) has been effectively demonstrated on a variety of archeological materials and is growing in use on

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archeological materials through a combination of portability, speed, and ease of use (Potts and West, 2008; Shugar and Mass, 2012). In order to assess the feasibility of using pXRF to differentiate between known geologic formations and potential for provenance analysis using FGV materials, samples of reference materials ($n = 239$) and archeological debitage ($n = 59$) were collected from throughout San Diego County (Table 1). The focus was on the Santiago Peak and Table Mountain Formations as they both contain fine-grained materials suitable for flaked stone production, have similar physical properties, and range in colors from green to black.

Promising results from the preliminary test of feasibility demonstrated that geochemical differentiation exists between Santiago Peak and Jacumba Volcanics, led to a full case-study of provenance analysis of archeological lithics in southern California. Analysis of archeological samples identified the surprising movement of FGV materials from the Otay Mesa area eastward into desert areas around Jacumba.

2. Relevant geological formations

The most commonly used lithic materials in archeological collection in San Diego County, through all periods of prehistory, has been volcanics. There are however several different volcanic formations, including both primary tabular deposits and secondary cobble deposits producing materials that include andesite, basalt, dacite, “felsite,” rhyolite, and metavolcanics (McFarland, 2000). Materials reported as felsite are often misidentified examples of Bedford canyon metasedimentary, Piedra de Lumbra (PDL) Chert, Lusardi Formation metavolcanics, or metamorphosed tuff found in various deposits.

2.1. Santiago Peak Volcanics

The dominant primary geologic unit in San Diego County is the Santiago Peak Volcanic formation (Fig. 1) that also contributes greatly to secondary cobble deposits throughout the county. The Santiago Peak Volcanics comprise an elongated belt of mildly metamorphosed volcanic, volcaniclastic, and sedimentary rocks that crop out from the southern edge of the Los Angeles basin southward into Mexico (Hanna, 1926; Kennedy and Peterson, 1975). The volcanic rocks range in composition from basalt to rhyolite but are predominantly dacite and andesite. The succession is typified by a wide variety of breccia, agglomerate, volcanic conglomerate, and fine-grained tuff and tuff breccia. They were originally named “Black Mountain Volcanics” for exposures in the northeast part of the area, but were re-named Santiago Peak Volcanics as the name “Black Mountain” was pre-empted (Hanna, 1926; Kennedy and Peterson, 1975; Larsen, 1948).

Table 1
Geologic formations and archeological sites sampled in this study.

Site	No. of samples
Reference samples	
Border Fields	20
Dictionary Hill	15
Lake Hodges	27
Lusardi Formation	16
Jacumba Road Grade	24
Otay Mesa 1	10
Otay Mesa 2	18
San Marcos Creek	25
Vista	17
CA-SDI-6776	10
CA-SDI-7030	18
CA-SDI-7060	18
CA-SDI-7074	11
CA-SDI-19303	10
Unknown archeological artifacts	
CA-IMP-103	12
CA-IMP-3784	6
CA-SDI-4788	4
CA-SDI-19018	1
CA-SDI-19281	20
CA-SDI-19293	1
CA-SDI-19304	4
CA-SDI-19364	4
CA-SDI-19851	5
CA-SDI-19853	2

The Santiago Peak Volcanics are hard and extremely resistant to weathering and erosion, occur along the Peninsular Range and foothills from the Santa Ana range in Baja California to Orange County, but is most common in the vicinity of Otay Mountain (see Dietler, 2004 Fig. 2) and form elevated peaks immediately east of the area at Black Mountain (Kennedy and Peterson, 1975; McFarland, 2000). This material varies widely in color, from light gray-green (sometimes incorrectly identified as felsite) to black, with most of the volcanic rocks exhibiting dark greenish gray where fresh and grayish red to dark reddish brown when weathered. Age estimates have varied from the Late Triassic, to the Mid-Cretaceous, but have been revised to the latest (Portlandian) Jurassic (Dietler, 2004; Fife et al., 1967; Kennedy and Peterson, 1975; Milow and Ennis, 1961).

2.2. Jacumba Volcanics

The “Jacumba Volcanics” or “Table Mountain Gravels” refers to a complex series of basaltic volcanic flows and dikes, cinder cones, ash deposits, volcanic debris flows, volcanic plugs, and breccias, forming thick (up to 500 feet thick) “piles” or mesa-like lava flows (May, 1976; Minch and Abbott, 1973). The mesa-like surfaces of Table Mountain represent erosional remnants of once-extensive lava flows, while the Mountain itself is sedimentary. Round Mountain, near Jacumba, is a remnant basaltic plug of an extinct volcano. Jacumba Volcanics are exposed and accessible around the margins of Jacumba Valley and to the northeast in proximity to Table Mountain (Laylander and Christenson, 1994; May, 1976). The formation was deposited during the early Miocene approximately 18 Ma ago (Brooks and Roberts, 1954; Strand, 1962; Todd, 2004).

The Jacumba Volcanics overly the Table Mountain Formation and are often associated in exposures with the yellowish and reddish brown, medium to coarse-grained sandstones (Minch and Abbott, 1973). The Table Mountain Formation is the remnant of an extensive fluvial deposit and contains clasts of local granite, intrusive gabbro and mixed granitic–metamorphic rocks often used in thermal features such as hearths and roasting pits (Brooks and Roberts, 1954; May, 1976; Strand, 1962). Lithics used for the production of chipped tools include fine-grained basalts of black and gray, porphyritic andesites, as well as low-grade green metavolcanics and metasedimentary rocks. These latter greenish rocks are similar in appearance to and often confused with Santiago Peak Volcanics, but are generally of lower quality and rarely exist in clasts larger than 30 cm, though this original size does little to help archeologists examining finished tools or debitage (May, 1976; Minch and Abbott, 1973).

2.3. Lusardi Formation

The Lusardi Formation has presented an interesting challenge to archeologists in San Diego County. The formation itself comprises an alluvial fan deposit of reddish brown cobble and boulder conglomerate with muddy sandstone interlayers, with outcrops in east Carlsbad, Rancho Santa Fe, east Poway (Poway Grade), northeast of San Vicente Reservoir and Alpine, dating to approximately 90–75 Ma ago (Abbott, 1999; Nordstrom, 1970). The largest and most abundant clasts include coarse-grained diorite, quartz diorite, and medium-grained granodiorite, as well as a variety of very fine-grained, greenish-gray, and dark-gray metamorphosed tuff (Kennedy and Peterson, 1975). Some of these clasts exhibited finely crenulated flow-banding, while others are very fine-grained black hornfels and volcanic rocks. The combination of sedimentary, metamorphosed, and volcanic materials intermingled

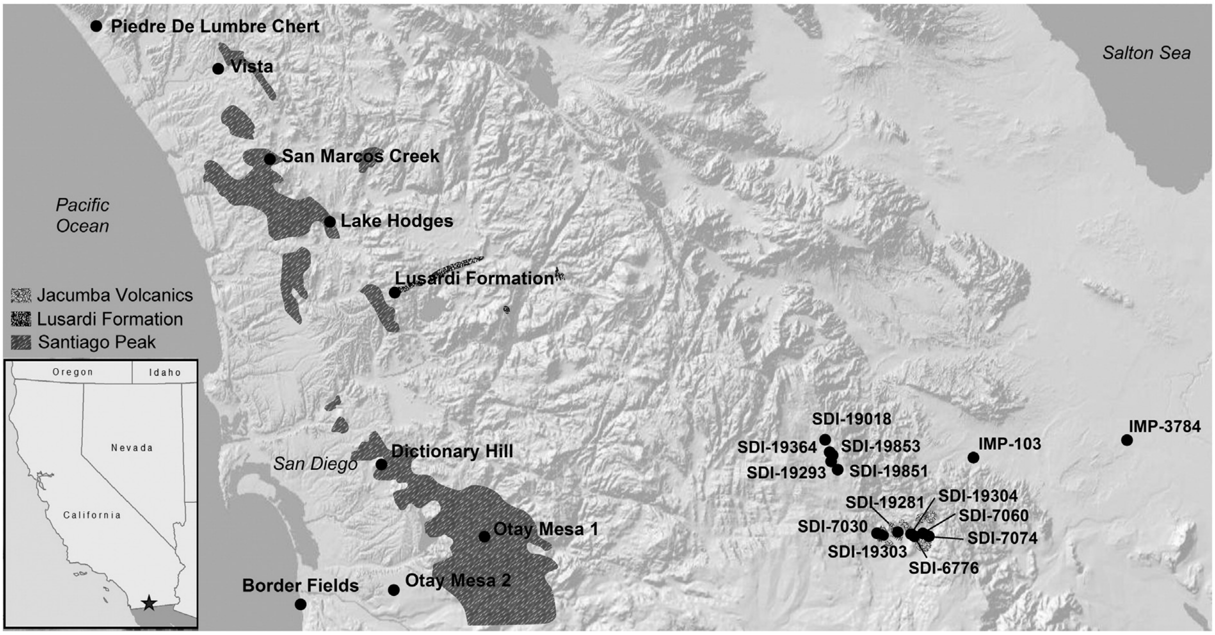

Fig. 1. Approximate locations of the sampling locations for geologic formations and archeological sites referred to in this study.

with small outcrops of higher quality lithic toolstone in the Poway area made it unclear if this area should be included with Santiago Peak Volcanics, or another geological unit.

From the beginning of archeological research in San Diego (circa 1930's) various authors have described materials from the Lusardi Formation (Pigniolo, 2009); a "blue and white banded quartzite" was identified by Roger's (ca. 1930's); a "black banded metavolcanic" was described by Day (1980a,b); Kaldenberg (1976) observed a quarry site of "andesite" near Poway; while Heuett (1980:37) clearly identified Rogers's "blue banded quartzite" as a distinctive lithic material, very few studies have recognized the material as unique, or attributed it to the Lusardi Formation. Identifications of the rock type and geologic formation have proven difficult for many archeologists. Materials that exhibit the distinctive flow-banding can be easily attributed to the Lusardi Formation near Poway (see Pigniolo, 2009 Fig. 4); however, darker volcanic samples and the greenish-gray metamorphosed tuff samples are visually similar to Santiago Peak Volcanics and cannot be readily distinguished. Being able to distinguish between these formations, and identifying any relevant geochemical sub-groups, would greatly aid in researcher's abilities to assess localized patterns of material procurement, movement, and interaction beyond the simple presence/absence of exotic artifacts.

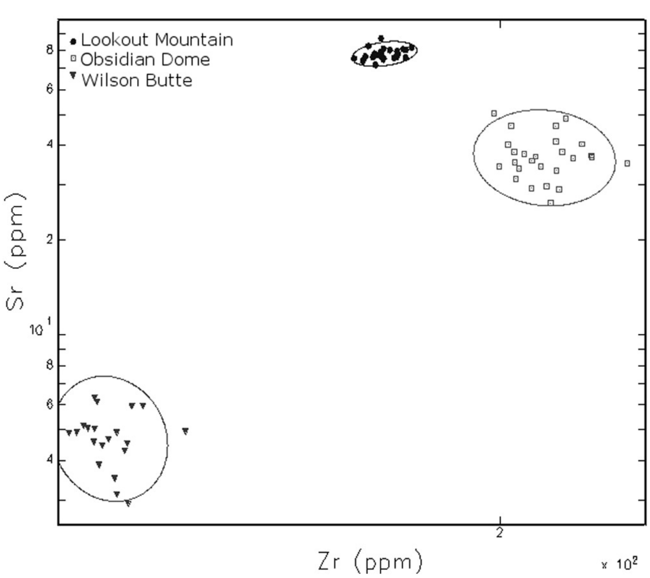

Fig. 2. Bivariate plot of zirconium and strontium XRF results for Long Valley Caldera rhyolite samples. 95% (2σ) confidence ellipses.

2.4. Previous regional geochemical studies

Given the range of rock types present in each of these formations, it is possible that the compositional properties of tool-grade stone within each source area will be distinguishable based on more accurate rock classifications. For example, andesites and basalts are Ca-, Na-, Al-rich due to plagioclase (e.g., Plagioclase feldspar group — $NaAlSi_3O_8$–$CaAl_2Si_2O_8$) and they have spikes in ferromagnesian minerals from amphiboles (e.g., Hornblende amphibole — $Ca_2(Mg, Fe, Al)_5$ $(Al, Si)_8O_{22}(OH)_2$) and pyroxenes (e.g., Hypersthene pyroxene — $(Mg,Fe)SiO_3$). Basalts are expected to have high Si, Al and Ca or Na because they are mainly plagioclase and they will have different spikes in Fe, Mg, Ca and Al, according to the type of inclusions. Rhyolites and rhyodacites are quartz and K-feldspar (orthoclase, microcline) and expected to be comprised of Si, K and limited trace/rare earth elements. Geochemical provenance analysis would certainly function effectively if it could identify the correct type of rock and only certain types of rocks were being used from each formation.

Geochemical work covering portions of the Jacumba Valley during geophysical studies of neighboring fault zones in northern Baja California and the Peninsular Ranges (Farquharson, 2004; Nelson, 1977; Parrish, 1990; Shaw et al., 2003; Springer, 2010; Todd et al., 2014), has demonstrated a number of geologic deformations that suggest promising levels of geochemical differentiation. The overall level of complexity in the eastern portion of San Diego County is higher than the west in terms of volcanic formations, but the majority of them are granitic structures that have not produced fine-grained rock suitable for tool production. Based on reconstructions of the formation history, elements such as Sr and Rb could potentially work as marker elements to distinguish the Table Mountain formation from others in the region (Parrish, 1990).

Gorzolla (1988) conducted a geochemical and petrographic analysis of Santiago Peak Volcanics along the western edge of the Peninsular

Ranges batholith, from roughly Riverside down to the Mexican Border. Results indicated a spatial distinction between two groups of volcanic rocks, with tholeiitic rocks (basalts and andesites) with higher concentrations of FeO* and TiO_2 more abundant to the south and calc-alkaline rocks (rhyolites and dacites) with lower values of MgO, CaO, and $Al2_2O_3$ prevalent to the north. The boundary for these two groups is approximately the southeastern corner of Camp Pendleton near Fallbrook, with some additional east–west gradation of samples. All of the samples included in this study came from within the southern tholeiitic zone.

Geologic maps for the region indicate likely geochemical differences based on localized formations and dominant rock types throughout areas such as the Jacumba Valley and Santiago Peak; however, these maps do not necessarily indicate the relative structure or quality of the rocks that will be accessible on the surface as part of a dominant formation, or indeed as isolated or intrusive portions of unrelated geological units. Thus, there is good reason to believe that relevant geochemical differences potentially exist at both the intra- and inter-site level for FGV geologic formations in this portion of southern California that would support the feasibility of archeological provenance studies.

3. Methods

Non-destructive Energy-Dispersive X-ray Fluorescence (ED-XRF) spectrometry is a well-established method to chemically characterize archeological lithics, primarily obsidian and basalt, and increasing attempted for more heterogeneous materials such as ceramics and sediments, though with mixed results (Hunt and Speakman, 2015; Potts and West, 2008; Shugar and Mass, 2012; Speakman et al., 2011). With the advent of the portable X-ray Fluorescence (pXRF) spectrometer, archeologists are now able to reliably conduct non-destructive artifact analyses in-situ as well as in the laboratory (Craig et al., 2007; Goodale et al., 2012; Liritzis and Zacharias, 2011; Potts and West, 2008; Shackley, 2010).

XRF operates using the interaction of primary X-rays with the sample, generating a range of secondary X-rays that have energy characteristic of the elements in the sample (Henderson, 2000; Pollard et al., 2007; Potts and West, 2008; Shugar and Mass, 2012). The primary X-rays hit the surface of the sample, excite the atoms within, and create inner-shell (K, L, M) vacancies in the atoms of the surface layers. The X-rays knock out inner-shell electrons and secondary X-rays are generated as electrons from outer shells lose energy when the drop down to fill the vacancies, emitting energy specific to the element from which they came, ranging from 0.1 to 50 Å. The secondary X-rays hit a detector that converts the pulses of the X-ray energies into electrical pulses corresponding to the different energies associated with the number of protons and thus of specific elements.

The analysis was performed at ASM Affiliates in Carlsbad, CA using the Bruker TRACeR III-V hand-held X-ray Fluorescence (pXRF) spectrometer. Artifacts and source materials were exposed to 3 min of X-ray emissions using 40 kV (voltage) 18 micro amps (current) using an aluminum (50 μm), copper (150 μm), and titanium (300 μm) filter. The filter was designed to maximize the data yield for pXRF used on obsidian samples. The filter used is likely not the most effective for lower silicic FGV, but was employed in this case-study specifically because many of the targeted materials are silica-rich microcrystalline matrices, obsidian standards were used to calibrate the data, and relevant comparable spectra were needed.

Elemental concentrations were generated using a calibration developed by Bruker, Missouri University Research Reactor (MURR), and the University of Georgia Center for Applied Isotope Studies based on a variety of analyzed obsidians from around the world ($n = 40$) (Glascock and Ferguson, 2012; Speakman, 2012). The calibration relies on the fundamental-parameters approach, based upon the theoretical relationship between measured X-ray intensities and the concentrations of elements in the sample, which should in principle provide the best-possible quantification results (Conrey et al., 2014; Jenkins, 1995; Sherman, 1955; Tertian and Claisse, 1982; van Sprang, 2000). Calibration samples were selected to provide a broad range of element concentrations from high-to-low, especially for elements that have proven useful in obsidian sourcing by XRF. Elements measured by this procedure include Mn, Fe, Rb, Sr, Y, Zr, and Nb. Most of these elements are particularly useful discriminating elements for obsidian source studies because, as large ions, they are incompatible with crystallizing solids; as magmas evolve the concentrations of incompatible elements will be different for each source.

Elemental concentration data were examined using a combination of exploratory multivariate statistical analytical techniques including bivariate plots, principal component analysis, and Mahalanobis distance classification (Baxter, 1994, 2003; Beier and Mommsen, 1994; Bieber et al., 1976; Bishop and Neff, 1989; Harbottle, 1976; Leese and Main, 1994; Neff, 1994, 1998; Sayre, 1975). The use of multiple techniques provides verification and cross-validation of all the conclusions.

4. Methodological demonstration of potential

The extent to which an artifact can be successfully used for provenance research varies depending on the material used and analytical technique employed (Neff, 1998, 2002; Weigand et al., 1977). Geochemical analytical techniques such as XRF operate at specific scales of analysis that generally define what materials can or cannot produce a useable dataset. Archeological obsidian is predominantly analyzed using XRF due to the homogenous chemical structure within samples, significant differentiation between individual geologic formation, and ease of analysis. The main limitations for obsidian are access to suitable comparative data for a given archeological collection, and the size of the recovered flakes. Obsidian is amenable to the production and refinement of very thin and very sharp edges and flakes as well as various sized blade technologies. The resultant lithic assemblage often includes many very thin pieces that cannot always meet the basic assumption of infinite thickness necessary for a fully accurate XRF assessment of desired elements within a given sample (Ferguson, 2012; Lundblad et al., 2008).

Other lithic materials are also prone to similar problems in archeological assemblages as the result of reduction strategies. Obsidian is known for remarkable geochemical homogeneity, largely as a result of the rapidity with which formations erupt and cool. Other volcanic materials often cover larger spatial areas and include greater numbers of discrete outcrops that can potential exhibit geochemical variability. The relative toughness of other FGV lithics such as rhyolites and metavolcanics renders them less likely to produce an abundance of very thin debitage, while low-silicic basalts and similarly tough materials are often shaped by and employed for grinding rather than flaking, producing suitably large artifacts. Analyses of FGV materials in archeological assemblages have met with varied success due to the vagaries of inter-source homogeneity in some cases, and intra-source heterogeneity in others (Clark et al., 1997; Gauthier and Burke, 2011; Hermes et al., 2001; Hermes and Ritchie, 1997a,b, Bertini et al., 2011; Jones et al., 1997, 2003, 2012; Latham et al., 1992; Lundblad et al., 2011; McAlister, 2011; Mills et al., 2010; Parker and Sheppard, 1997; Sitko, 2009; Tripati et al., 2010; Weisler and Kirch, 1996; Williams-Thorpe et al., 1999). The level of internal compositional heterogeneity can render ineffective proven techniques simply due to the presence of underlying layering or phenocrysts within a geologic sample or archeological artifact.

The volcanic materials described for San Diego Country are relatively high-silicic species that often contain visible phenocrysts. To assess the potential of pXRF on the materials in question, several samples of rhyolite were analyzed that have been previously investigated by LA–ICP–MS (Scharlotta, 2010). Rhyolite samples from three geologic formations (Lookout Mountain, Obsidian Dome, and Wilson Butte) within the Long Valley Caldera system in eastern California were specifically chosen because they had helped to demonstrate the feasibility of using nonobsidian rhyolite for archeological provenance and were originally calibrated using obsidian and glass standards (NIST SRM-612, SRM-610, Glass Buttes, Medicine Lake, Obsidian Butte, Bodie Hills, Queen, Fish Springs). Glass Buttes and Medicine Lake are included in the 40 obsidian sources used by Bruker to calibrate materials analyzed by pXRF. Calibration of the LA–ICP–MS data follows a different statistical procedure, using graded standards whose concentration brackets the expected concentration and whose matrix composition is similar to the sample unknowns (Bertini et al., 2011; Cochrane and Neff, 2006; Eckert and James, 2011; Glascock, 1992; Golitko et al., 2012; Springer, 2010; van Elteren et al., 2009). This approach is similar to the method introduced by Gratuze (1999) and Gratuze et al. (2001).

Long Valley Caldera rhyolite samples were initially chosen due to their geographic proximity to one another in order to demonstrate the efficacy of geochemical analysis in an environment of related formations. Much of the Long Valley Caldera shares a magma source; however, the complex eruption history and repeated recharge of the magma chamber in between eruptions has produced a series of geochemically distinct formations.

The goal was to use these source materials to help calibrate other FGV materials either in addition to, or in lieu of obsidian samples with a different matrix. Analysis of the Long Valley Caldera rhyolite samples produced promising initial results (Fig. 1), with excellent group discrimination. A comparison of the calibrated ppm values produced from the XRF analysis, to those from the LA–ICP–MS study (Table 2, Supplementary Table I), identified significant differences in reported values beyond what could be explicable by limited matrix effects, or variation in the calibration using different obsidian reference materials. While data are presented in ppm format, they should rightly be considered as relative data due to potential matrix effects and the use of a high-silica standard calibration as opposed to material-specific standards. Accurate quantification is not necessary for an internally coherent comparative analysis, but will have to be repeated using more suitable FGV reference materials before the data could be used for broader research. It is beyond the scope of the current study to determine if the departure in datasets was due to differing calibration processes, reference materials, intra-sample composition heterogeneity at the scale of the pXRF analysis which is larger than the LA–ICP–MS groundmass study, or another cause.

5. Reference and archeological samples

After verifying that FGV materials such as the Long Valley Caldera rhyolites could be effectively discriminated from one another, samples from the relevant formations in San Diego County, and archeological specimens from sites in San Diego and Imperial Counties were analyzed.

Source materials comprising 132 samples from seven locales of the Santiago Peak formation were collected that are broadly representative of the extent of the formation in San Diego County. As shown in Fig. 1 and Table 1, 17 samples were analyzed from a site near Guajome Lake north of Vista, 25 samples from San Marcos Creek, 27 samples from three collection sites at the eastern edge of Lake Hodges, 15 samples from Dictionary Hill, north of Sweetwater Reservoir, 20 samples from Border Fields State Park near the border with Mexico, 10 samples from one site in the Otay Mesa Mountains (Otay Mesa 1), and 18 samples from Otay Mesa (Otay Mesa 2).

The Lusardi Formation is only accessible as a surface exposure suitable for prehistoric lithic quarrying in a limited area east of Poway. All samples were collected from an exposure near the intersection of Scripp's Poway Parkway and California Highway 67.

Volcanic materials from Jacumba Valley, the Jacumba Mountains, and the Yuha Desert appear to exhibit higher levels of weathering than materials observed in other portions of San Diego County. The reasons for this could be related to either the structure of the rocks themselves, or differences in localized weather conditions east and west of regional mountains. This difference in chemical weathering can impact the efficacy of XRF analysis (Bieber et al., 1976; Parrish, 1990; Potts et al., 2006; Sitko, 2009), and potentially impact the effectiveness of an experimental case-study. In order to account for suspect problems that could result from comparing archeological materials with weathered reference samples, or freshly broken reference samples of different materials than those used in prehistory, a two-stage collection strategy was employed. Raw materials from a new road grade near Jacumba were collected in tandem with archeological work in the Jacumba Valley. These materials were not weathered, having been recently exposed. Given the number of archeological sites composed of volcanic lithic assemblages (e.g., CA-SDI-6776, -7030, -7060, -7074, and -19303), additional reference materials were deemed necessary for the analysis. Preliminary analysis of numerous lithics from archeological assemblages proved strongly similar to the reference materials, so these collections were used as reference sample collections after verification of local origins through XRF analysis as compared with unmodified cobbles collected in proximity to archeological sites. Fig. 3 shows a comparison of reference materials collected in road grades and in proximity to archeological sites in the Jacumba Valley, with materials recovered as debitage in archeological assemblages. The shape of the ellipses is slightly offset by the archeological outliers, most likely caused by inadvertent analysis of phenocrysts along with the targeted groundmass of samples.

Table 2
A comparison of the mean and standard deviation values for XRF and LA–ICP–MS analysis of Long Valley Caldera rhyolite samples.

pXRF	Mn	Fe	Rb	Sr	Y	Zr	Nb
Lookout Mtn — mean	307	8927	135	78	17	167	14
Lookout Mtn — std dev	68	227	3	3	1	4	1
Obsidian Dome — mean	382	10,886	152	37	26	215	19
Obsidian Dome — std dev	39	493	3	6	2	11	1
Wilson Butte — mean	295	7589	176	5	26	108	21
Wilson Butte — std dev	41	141	4	1	1	4	1
ICP–MS	**Mn**	**Fe**	**Rb**	**Sr**	**Y**	**Zr**	**Nb**
Lookout Mtn — mean	538	18,760	146	251	16	318	–
Lookout Mtn — std dev	477	18,752	46	567	8	272	–
Obsidian Dome — mean	441	13,009	184	17	17	227	–
Obsidian Dome — std dev	47	2425	29	15	2	22	–
Wilson Butte — mean	455	11,005	208	9	13	66	–
Wilson Butte — std dev	110	2769	13	7	2	13	–

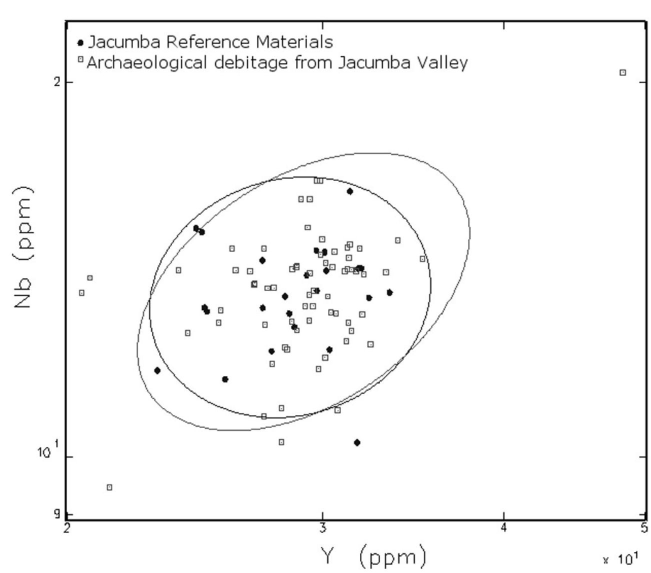

Fig. 3. Bivariate plot of yttrium and niobium XRF results for Jacumba Valley reference and archeological samples. 95% (2σ) confidence ellipses.

Archeological samples were drawn from a series of projects in and around the Jacumba and McCain Valleys, Jacumba Mountains, and the Yuha Desert conducted by ASM Affiliates, Inc. (e.g., Scharlotta et al., 2012; Speakman and Shackley, 2013; Williams et al., 2014a,b). The materials were composed of debitage or tools showing only limited retouch, as the most representative aspect of the lithic assemblage in terms of total raw material use, as well as a lack of refined tools for analysis. Given the relative ease of access to volcanic raw materials in San Diego and Imperial Counties, it was hypothesized that only refined tools would likely travel significant distances through direct movement of the owner or through trade.

6. Table Mountain, Otay Mesa, and Lusardi Formations

The collection of samples from archeological sources for use as reference materials of the Table Mountain Volcanics near Jacumba presented the first challenge to a regional comparison of FGV materials in this analysis. The archeological samples with unknown provenance were drawn from the southeastern portion of San Diego County and the western portion of Imperial County. Thus, the likely sources of raw materials would be those accessible in the southern portions of San Diego County, unless a significant amount of materials were being moved over long distances in prehistory. After demonstrating the relative homogeneity of volcanics from near Jacumba (Fig. 3), the next step was determining the extent of intra-formation chemical variability in the Santiago Peak Formation accessible in southern San Diego County.

Three sampling areas related to Otay Mesa were chosen due to the variety of raw material exposures possible. The largest geologic body attributed to the Santiago Peak Formation is approximately the boundaries of the Otay and Jamul Mountains. What is less clear is the extent to which erosional or secondary deposits deriving from these mountains have influenced surficial geology in areas to the west. Geological maps (e.g., Dietler, 2004; Strand, 1962) characterize areas west of the Otay/San Ysidro Mountains as primarily consisting of Eocene cobbles and Quaternary marine terraces that include a variety of different rocks. A comparison of samples drawn from the mountains, foothill mesa, and volcanic cobbles carried downstream and accessible near the beach showed a high degree of overlap (Fig. 4). Due to the level of overlap, these three groups were combined into a single Otay Mesa group for further analysis.

Expanding the analysis to include multiple formations, it became clear that there was a potential problem with compositional overlaps

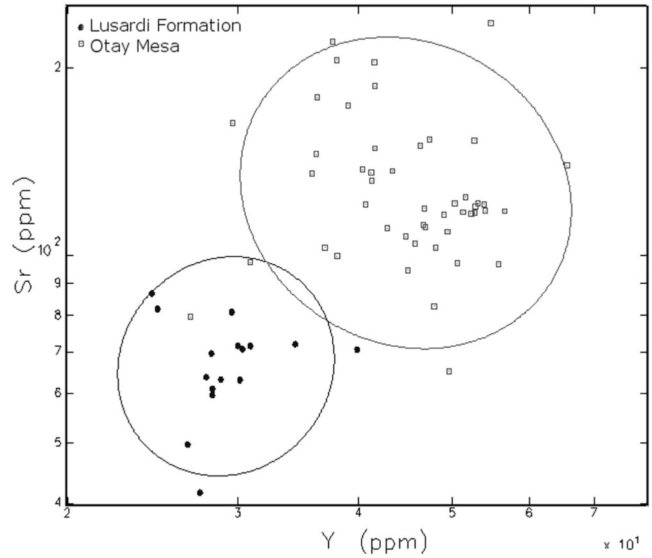

Fig. 5. Bivariate plot of yttrium and strontium XRF results for Otay Mesa and Lusardi Formation reference samples. 95% (2σ) confidence ellipses.

between the Otay Mesa and Lusardi Formation groups (Fig. 5). The level of overlap varied by element, but could provide enough ambiguity to make provenance determinations difficult. Using canonical discriminant analysis, the degree of overlap between the two sources is reduced to a level beyond 2σ (Fig. 6), which is less than 5% likelihood of overlap, with the addition of a hyperspatial directionality that increases the likelihood of correction group assignment for samples falling within the range of uncertainty.

7. Analysis of unknown artifacts

After suitably addressing potential concerns for intra-formation compositional variability for Table Mountain Volcanics near Jacumba, Santiago Peak Formation materials in Otay Mesa, and the Lusardi Formation, the analysis could progress to provenance determination for the 59 archeological samples. Fig. 7 shows the results of using Principal Components Analysis (PCA), archeological artifacts fell into three categories based on visual exploratory statistics. The majority of

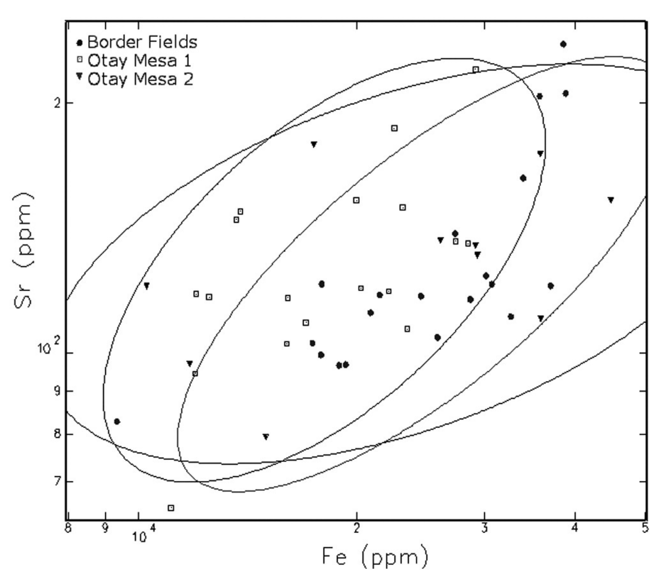

Fig. 4. Bivariate plot of iron and strontium XRF results for Otay Mesa 1, Otay Mesa 2, and Border Fields reference samples. 95% (2σ) confidence ellipses.

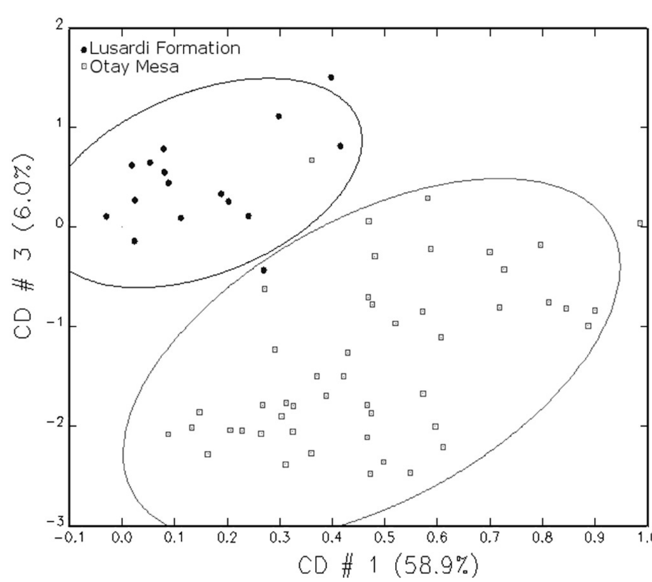

Fig. 6. Bivariate plot of canonical discriminant analysis differentiating Otay Mesa and Lusardi Formation reference samples. 95% (2σ) confidence ellipses.

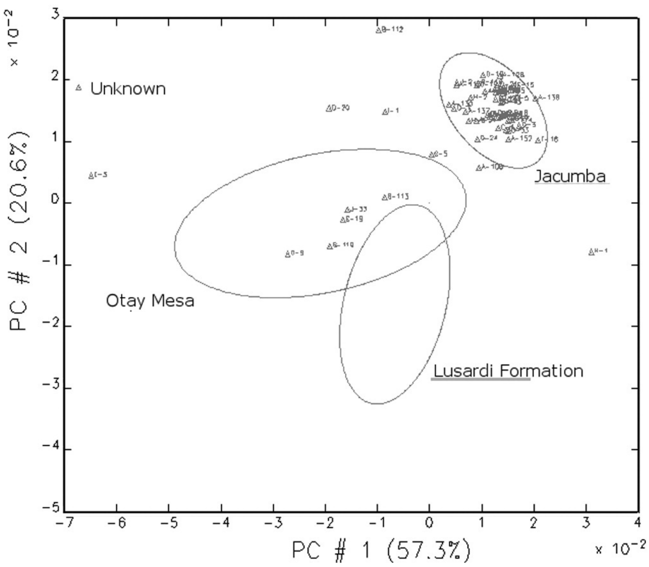

Fig. 7. PCA analysis results of archeological samples projected against Principal Components 1 and 2 for source groups near Jacumba, Otay Mesa, and the Lusardi Formation.

artifacts were composed of Table Mountain Volcanics like those found in Jacumba Valley. Second, five artifacts fell into the center of the range for Otay Mesa. The third group is composed of seven outliers, samples falling outside of the 2σ ranges for the three comparison groups, most likely due to internal compositional variation and/or the presence of phenocrysts within the analyzed portion of the sample. Principal components cover the dominant ranges of variation composed of multiple individual elements, so errant data on a single element are likely not responsible for producing outliers in multivariate space. The scattering of the outlier samples does not suggest the presence of additional source groups not covered by the reference materials used in this analysis.

To verify the visual observations from exploratory statistics, group membership probabilities based on Mahalanobis Distances were calculated for the archeological samples (Table 3). A total of 13 samples were identified as being from groups other than Jacumba, or non-local materials. Based on the PCA results suggesting five samples from Otay Mesa and seven outliers, one additional sample was identified as being either problematic or non-local in origin. These thirteen samples were projected against single-element biplots to examine the results (Fig. 8). Although the group determination identified all but one of the non-Jacumba samples as being most closely related to the Lusardi Formation group, it is clear that this is not the case as none of the samples assigned to the Lusardi group are either black in color, or contain the distinctive flow-banding.. Six samples are from Otay Mesa without additional verification, with a seventh likely. Examining the

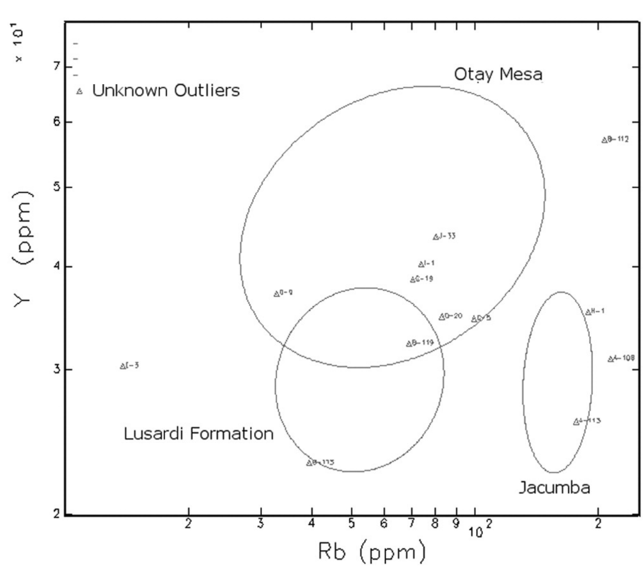

Fig. 8. Outlier results of archeological samples projected against rubidium and yttrium for source groups near Jacumba, Otay Mesa, and the Lusardi Formation.

Table 3
Provenance results (Mahalanobis distance group membership probabilities) for archeological samples projected against source groups from Santiago Peak (near Otay Mesa), the Lusardi Formation, and Table Mountain (near Jacumba).

Membership probabilities (%) for samples from the group: Unknown probability for each sample calculated after removal from original group.				
Sample ID	Jacumba	Lusardi	Otay mesa	Best group
IMP-103-27	87.20	0.10	<0.01	Jacumba
IMP-103-53	32.89	0.08	0.02	Jacumba
IMP-103-54	9.68	0.02	<0.01	Jacumba
IMP-103-64	12.63	0.08	<0.01	Jacumba
IMP-103-81	17.04	0.17	0.04	Jacumba
IMP-103-106	<0.01	0.57	<0.01	Lusardi
IMP-103-113	0.01	0.14	<0.01	Lusardi
IMP-103-128	85.19	0.05	0.01	Jacumba
IMP-103-130	78.86	0.11	<0.01	Jacumba
IMP-103-136	2.28	0.18	0.34	Jacumba
IMP-103-137	19.93	0.34	0.08	Jacumba
IMP-103-152	95.03	0.09	0.01	Jacumba
IMP-3784-112	<0.01	0.17	0.05	Lusardi
IMP-3784-113	<0.01	0.04	<0.01	Lusardi
IMP-3784-114	99.43	0.10	0.01	Jacumba
IMP-3784-115	86.58	0.06	<0.01	Jacumba
IMP-3784-116	69.20	0.03	<0.01	Jacumba
IMP-3784-119	<0.01	8.56	<0.01	Lusardi
SDI-19018-1	72.93	0.07	<0.01	Jacumba
SDI-19281-1	31.86	0.05	<0.01	Jacumba
SDI-19281-2	87.84	0.19	0.12	Jacumba
SDI-19281-3	0.81	0.10	<0.01	Jacumba
SDI-19281-4	95.82	0.11	<0.01	Jacumba
SDI-19281-5	69.80	0.11	0.04	Jacumba
SDI-19281-6	65.50	0.12	0.01	Jacumba
SDI-19281-7	62.96	0.09	<0.01	Jacumba
SDI-19281-8	58.88	0.12	0.04	Jacumba
SDI-19281-9	<0.01	3.69	0.29	Lusardi
SDI-19281-10	80.91	0.08	0.01	Jacumba
SDI-19281-12	65.40	0.08	<0.01	Jacumba
SDI-19281-15	68.38	0.06	<0.01	Jacumba
SDI-19281-16	73.51	0.07	<0.01	Jacumba
SDI-19281-17	18.27	0.05	0.01	Jacumba
SDI-19281-19	74.63	0.07	0.02	Jacumba
SDI-19281-20	<0.01	0.08	0.05	Lusardi
SDI-19281-21	91.84	0.04	0.01	Jacumba
SDI-19281-24	30.85	0.08	0.01	Jacumba
SDI-19281-33	87.68	0.23	0.01	Jacumba
SDI-19281-34	93.44	0.15	0.03	Jacumba
SDI-19293-3	<0.01	<0.01	<0.01	Lusardi
SDI-19304-13	2.38	0.07	0.03	Jacumba
SDI-19304-14	77.62	0.10	0.03	Jacumba
SDI-19304-15	3.13	0.04	0.01	Jacumba
SDI-19304-16	7.29	0.11	<0.01	Jacumba
SDI-19364-18	99.92	0.09	<0.01	Jacumba
SDI-19364-19	<0.01	4.16	93.25	Otay mesa
SDI-19364-21	86.57	0.03	<0.01	Jacumba
SDI-19364-5	0.01	0.22	<0.01	Lusardi
SDI-19851-1	<0.01	0.06	<0.01	Lusardi
SDI-19851-2	71.19	0.14	0.02	Jacumba
SDI-19851-5	42.77	0.10	<0.01	Jacumba
SDI-19851-9	71.04	0.06	<0.01	Jacumba
SDI-19851-10	85.27	0.07	0.02	Jacumba
SDI-19853-1	<0.01	0.06	0.01	Lusardi
SDI-19853-11	93.94	0.14	<0.01	Jacumba
SDI-4788-2	14.26	0.02	<0.01	Jacumba
SDI-4788-6	28.36	0.25	0.42	Jacumba
SDI-4788-12	98.33	0.11	<0.01	Jacumba
SDI-4788-33	<0.01	3.12	0.79	Lusardi

single sample with only Otay Mesa and Lusardi reference groups, it appears that the sample is more closely associated with Otay Mesa, but that the data suggest the presence of phenocrysts or other internal variability. Three of the outliers appear closely related to the Jacumba group, with one sample falling within the confidence ellipse itself.

Three samples still cannot be assigned to a group and would need to be re-analyzed to determine if their internal geochemical composition were generally too variable, or if an unseen phenocryst were behind the spot analyzed, skewing the results. The overall results of the analysis are quite good, with 56 of 59 (94.9%) of unknown artifacts assigned to a source group that seems correct given both their visual and geochemical composition. Given the lack of homogeneity in visual structure, it was unlikely that geochemical analysis would be able to produce good provenance results for all samples, though this is often true for proven materials such as obsidian.

8. Subdividing Santiago Peak

Given the success of the main goals of this research, one additional avenue of inquiry was pursued: to what extent can the Santiago Peak Formation be subdivided into geochemically distinct regions? The extension of the study was aimed to determine more fully the extent to which geochemical provenance research is feasible using pXRF on southern Californian FGV materials. As noted, portions of the Santiago Peak Formation in southern San Diego County show broad compositional overlap and are more easily viewed as a single geochemical group with some degree of internal variability that could potentially limit provenance research. What is less clear is the extent to which different exposures of the formation throughout the county, or indeed in neighboring areas of Orange County and Baja California. To explore this question, samples of Santiago Peak materials were collected from seven areas spanning San Diego County, from Otay Mesa along the southern border to north of Vista.

For this portion of the study the three areas near Otay Mesa (Border Fields, Otay Mesa 1 and 2) were combined into a single group. The consolidation of these groups follows the assumption that the latter two groups represent secondary deposits from the Otay Mesa 1 portion of the Santiago Peak Formation as is suggested by sediment and geological maps of the area. Similarly, all samples collected near Lake Hodges were grouped together into a single representative group as they accessed different outcrops of the same exposure in close proximity. Future research involving more intensive micro-regional sampling may help to clarify the degree of geochemical variation within the Santiago Peak Formation and lend credence to ungroup different clustered samples, but evidence available at present does not support such an approach.

With Santiago Peak divided into five sub-groups (Dictionary Hill, Lake Hodges, Otay Mesa, San Marcos Creek, and Vista), there appears to be a high degree of overlap with indications of a degree of discrimination between the different sub-groups (Fig. 9). Clouding the ability to separate out geographically distinct groups, is the wide range of chemical variability covered by the San Marcos Creek and Vista groups. Repeating the exercise using discriminant analysis (Fig. 10), the Dictionary Hill, Lake Hodges, and Otay Mesa groups can be parsed out fairly well, though not at a 2σ level. Samples of Santiago Peak volcanics with unknown origin could very likely be attributed to a single source area within the southern half of San Diego County, with additional steps of verification using specific elemental combinations for samples falling into overlapping areas.

Prospects for Santiago Peak volcanic deposits in the northern portion of the county seem less rosy. The higher level of composition variation in the San Marcos Creek and Vista source groups may reflect the nature of the deposits as secondary cobble fields, readily available in drainages. Archeological populations are not likely to have sought out primary deposits for a material source when secondary cobbles are easily accessed in creek and riverbeds, unless there is a material advantage to accessing a primary outcrop. There is no clear evidence of higher quality materials being available solely from primary deposits, though it remains possible that future research on archeological materials could indicate the preference for a specific quarry locale for certain tool types (e.g., projectile points).

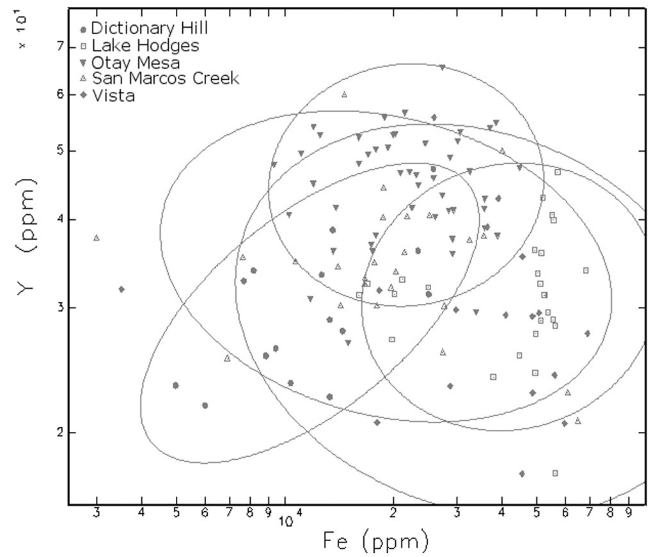

Fig. 9. Bivariate plot of iron and yttrium XRF results for Santiago Peak reference samples from five sampling areas. 95% (2σ) confidence ellipses.

9. Conclusions

Looking at the full range of geochemical variability within exposures of the Santiago Peak Formation accessible in San Diego County, it is difficult to be optimistic for the full potential of using XRF to adequately provenance FGV in the region. In contrast, reasonably good grouping between groups accessible as primary deposits, or secondary cobble fields attributable to a portion of the larger formation can be demonstrated. This suggests the likelihood that terms like Santiago Peak volcanics or metavolcanics have been applied too loosely when describing archeological lithic raw materials and that other volcanic material

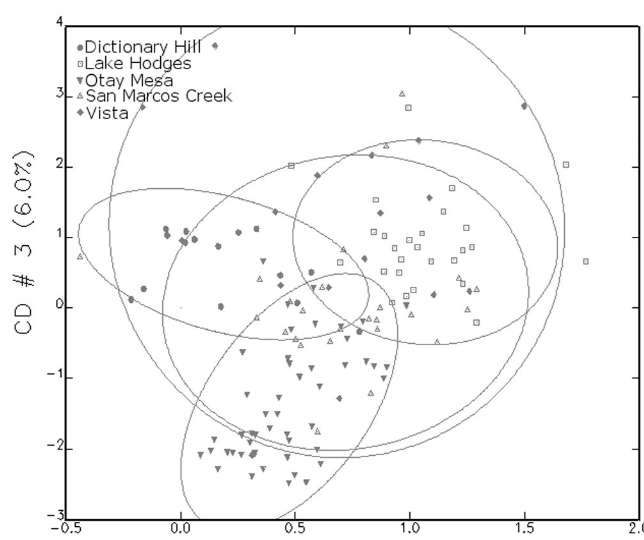

Fig. 10. Bivariate plot of canonical discriminant analysis of XRF results for Santiago Peak reference samples from five sampling areas. 95% (2σ) confidence ellipses.

accessible as cobble float are being intermixed with Santiago Peak volcanics at least in northern portions of San Diego County.

An analysis of 59 archeological artifacts originally identified as being local volcanic materials indicated that this was largely correct; however, seven artifacts were produced from Santiago Peak materials most closely associated with Otay Mesa. This demonstrates that a limited degree of material flow was occurring in a west–east direction in the San Diego region, an intriguing result given the accessibility of raw materials in the area. Evidence of long-distance trade including exotic materials such as obsidian from Obsidian Butte and Wonderstone on the shores of the Salton Sea and cryptocrystalline materials from desert sources are well documented in southern California, but the movement of lower grade materials received less discussion.

Using more defined source groups such as those from Otay Mesa and Dictionary Hill, Santiago Peak volcanics can be effectively discriminated from materials related to the Lusardi Formation and Table Mountain volcanics near Jacumba. Such a result is promising given the visual similarities between many of these materials, ranging in colors from green to black and similar amounts of visible phenocrysts. The tolerances for analysis of FGV materials containing phenocrysts and other non-conformities known to produce compositional heterogeneity are certain to be higher than homogenous materials such as obsidian or tool-grade basalts. The original goal was to ascertain the feasibility of conducted such research, which while imperfect has proven possible.

The combination of filter and settings used in this study are standard on all Bruker devices for analyzing obsidian. The use of matrix-matched calibrations would produce superior results and should be pursued further for future research. Rhyolite samples from the Long Valley Caldera system investigated for this role did not prove suitable in this case, though other rhyolite samples or other similar FGVs from southern California may prove effective for this role.

This case-study highlights the importance of research into new lithic materials where possible in testing long-standing hypotheses for human behavior. The abundance of volcanic materials accessible in primary and secondary deposits throughout the county and the lack of individual outcrops of materials with suitable quality to be in demand at a regional level has led to a general hypothesis that materials were locally procured unless demonstrably exotic in origins. As shown in the western Mojave Desert (Scharlotta, 2010) and again here, materials viewed as local or lower quality can provide invaluable insight into patterns of raw material procurement, population movement, and regional interactions. Ethnohistoric accounts and exotic archeological materials such as obsidian on the coast and shell in the interior suggest the movement of goods and interactions between populations; however, without this type of spatially refined tracking of movement in the archeological record, it is difficult to demonstrate direct connections between neighboring groups beyond evidence to suggest that they participated in similar regional or inter-regional trade networks. Reconstructing procurement, movement, and interaction at the regional level is critical to explanations related to the movement of exotic goods over long distances, for example differentiating systemized trade networks involving long distance travel by certain groups or individuals from more casual down-the-line types of trading interactions between neighboring populations.

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